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16. ABSTRACT

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Implications of a Gradient in Acid and Ion Deposition across the Northern Great Lakes States

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■ Average precipitation pH, 1979–1982, declines from west to east from 5.3 to 4.3 along a cross section of sites in Minnesota, Wisconsin, and Michigan. This answers questions about the seasonal and geographic pattern of anthropogenic acid precursor emissions and reaction products (SO_4^{2-}, NO_3^-, H^+, NH_4^+) that increase from west to east. Except for higher concentrations of Ca^{2+} and Mg^{2+} observed at one site in the cultivated area of southwestern Minnesota, the contribution of soil-related metal cations to the total ions in solution is small (17%) and relatively uniform across the region. Significant seasonal and geographic patterns in precipitation chemistry and deposition values are observed. Close correspondence of the sums of strong acid anions with the sums of hydrogen and ammonium ions in precipitation is observed, indicating anthropogenic sources of sulfur and nitrogen oxides. Present atmospheric inputs show close chemical correspondence when precipitation chemistry values are compared to the resulting ionic composition of weakly buffered lakes in north central Wisconsin and northern Michigan. The wet deposition of total acidity in the middle and eastern part of the region is comparable to that of impacted sites in the Adirondacks and in regions of Scandinavia.

Introduction

Much research on the phenomenon of acidic precipitation has focused on the Eastern United States, eastern Canada, and the southern regions of Scandinavian countries (*1–5*). Munger and Eisenreich (*6*), reviewing the recent precipitation chemistry data on a continental scale, noted wide variations in elemental concentrations from one region to another, sometimes over relatively short distances. Gorham et al. (*7*) have examined the ionic correlation in the Eastern U.S. and noted the relationship of wet acidic loadings to precipitation pH. The transition from acid-dominated to base-dominated precipitation across the Great Lakes States (GLS) was not addressed in detail in these papers. In recognition of the large area of sensitive soils and of the abundance of low alkalinity surface waters in northern Minnesota, Wisconsin, and Michigan (*8, 9*), three precipitation monitoring sites were established in the Boundary Waters Canoe Area Wilderness of Minnesota and the northern highland region of Wisconsin. The possible effects of acidic deposition on this region are the concern of resource managers in these states and of scientists in general.

Research on which compounds contribute most to the differences in precipitation chemistry values found across this region offers the potential to understand the significance of regional and local variation in pH, ionic compositions, acid-forming precursors, and their reactive products (SO_4^{2-}, NO_3^-, H^+, and NH_4^+). Soil- and agricultural-derived ions (*10–12*) also need to be considered as inputs to changes in surface water chemistry values relating to seasonal variations and historical changes in rainfall chemistry (*9, 13–15*). The objectives of this paper are, therefore, to report and evaluate the significance of geographic patterns in the ion composition of acidic and basic reactants in precipitation across the GLS region, to compare the potential significance of the snow period chemistry values with those of the rain period, to compare to wet deposition in other regions, and to compare the composition of precipitation with the resulting surface water.

Materials and Methods

Three precipitation monitoring sites were established in 1980 according to the protocol of the National Atmospheric Deposition Program (NADP) (*16*) bringing the total number of sites to eight in the western Great Lakes States (Table I). Weekly composite precipitation samples were collected by using Aerochem Metrics (Miami, FL) Model 301 automatic sensing wet/dry precipitation collectors. Field observations and measurements of environmental conditions were made according to NADP procedures (*16*), and a portion of the sample was used to measure pH and specific conductance. The remaining sample in the collection bucket was shipped to the Illinois Water Survey–Central Analytical Laboratory (CAL), Champaign, IL, for additional analyses. The concentrations of Ca, Mg, Na, and K were measured by using an Instrumentation Laboratory Model 353 atomic absorption spectrophotometer. Concentrations of sulfate, nitrate, chloride, and ammonium were measured colorimetrically on a Technicon Auto Analyzer II. Hydrogen ion was measured with an Orion Model 811 pH meter with Beckman electrodes and a Yellow Springs Instrument Co alternating current conductance bridge was used with a glass microelectrode, $K = 1$, for specific conductance measurements. Field and laboratory data were key punched and reported back to site investigators by CAL for checking and quality assurance and eventually were published by the NADP as Quarterly Reports (*17*).

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Table I. Average H^+ Concentration, Volume Weighted, Expressed as pH, from Weekly Composite Samples (Measured at CAL) over a 3-year Period at Eight Sites across the Western Great Lakes States[a]

site name location (N. lat., W. long.)	date site established	yearly average Dec 1979–Nov 1980 pH	N	Dec 1980–Nov 1981 pH	N	Dec 1981–Nov 1982 pH	N	snow period, Dec–March pH	N	rain period, April–Nov pH	N	all 3 years, Dec 1979–Nov 1982 pH	N
Lamberton, MN; 44°14′; 95°18′	Jan 2, 1979	4.99	31	5.38	33	5.45	36	5.01	15	5.27	85	5.25	100
Marcel, MN; 47°32′, 93°28′	July 6, 1978	5.07	38	5.11	44	4.99	44	4.85	38	5.09	88	5.05	126
Fernberg, MN; 47°57′, 91°30′	Nov 18, 1980	5.69	1	4.93	38	4.93	46	4.83	27	4.95	58	4.93	85
Spooner, WI; 45°49′, 91°53′	June 3, 1980	5.11	22	4.80	27	4.91	42	4.69	19	4.92	72	4.90	91
Trout Lake, WI; 46°03′, 39°39′	Jan 22, 1980	4.64	39	4.79	43	4.68	49	4.57	39	4.71	92	4.70	131
Douglas Lake, MI; 45°34′, 84°41′	July 3, 1979	4.33	42	4.43	40	4.44	48	4.39	42	4.41	88	4.40	130
Wellston, MI; 44°13′, 85°49′	Oct 10, 1978	4.33	44	4.32	43	4.40	49	4.37	46	4.35	90	4.35	136
Kellogg, MI; 42°25′, 85°24′	June 26, 1979	4.33	38	4.32	37	4.33	44	4.39	35	4.32	84	4.33	119

[a] The number of samples in each average for the period Dec 1979–Nov 1982 is shown (*N*).

Table II. Analysis of the pH Differences between Field Site Investigators and Laboratory Results (CAL), as a Function of Precipitation Sampling Event Depth and in Comparison with Other Measured Ions for the 3-year Period 12/79–11/82

location	no. of samples	mean pH, site	mean pH, CAL	$\Delta[H^+]$, site – CAL μequiv/L	SD	slope of log [ion, μequiv/L] vs. log (precipitation depth) H^+, site	H^+, CAL	SO_4^{2-}	NO_3^-	Ca^{2+}	Na^+
Lamberton, MN	84	4.63	5.33	18.9	38.7	+0.47	+0.63	−0.20	−0.27	−0.49	−0.59
Marcell, MN	114	4.88	4.99	2.9	8.2	−0.18	+0.30	−0.23	−0.22	−0.38	−0.60
Fernberg, MN	74	4.74	4.92	5.9	16.5	+0.09	+0.33	−0.22	−0.28	−0.45	−0.56
Spooner, WI	21	4.45	4.79	19.4	38.4	−0.14	+0.41	−0.15	−0.18	−0.35	−0.62
Trout Lake, WI	108	4.57	4.67	5.3	7.5	+0.08	+0.30	−0.13	−0.18	−0.33	−0.54
Douglas Lake, MI	117	4.30	4.39	9.4	21.7	+0.01	+0.23	−0.21	−0.36	−0.50	−0.60
Wellston, MI	115	4.16	4.35	24.7	55.9	+0.09	+0.37	−0.19	−0.18	−0.46	−0.62
Kellogg, MI	94	4.22	4.33	13.8	32.4	+0.11	+0.23	−0.13	−0.19	−0.32	−0.29

The data reported in this analysis were measured or obtained from CAL and the other individual site investigators in 1983. Analyses of normal wetside and dilute wetside precipitation samples were included, but trace precipitation and dryside samples were excluded. Over 900 pH values for weekly composites from the eight monitoring sites and over 5000 concentration values for the other ions were measured. Both the pH and specific conductivity measurements reported by the site investigators and by CAL have been used; the latter assure uniformity in technique and quality assurance for all chemical analyses (*18*, *19*).

To summarize, the data have been grouped into periods approximately corresponding to the dominant seasons in this region, the "winter" period (December–March) when snow accumulation occurs, the "nonsnow" or rain period (April–November), spring–summer (April–July), and summer–fall (August–November). Wet deposition was calculated by using rain gauge measurements rather than sample bucket volumes as the latter underestimate total precipitation volumes by about 4 ± 2% over all sites. Of the 670 weekly composite samples, only 29 (<0.5%) had one or more missing values for individual ion measurements. Calculation of the missing ion values was computed by using a linear regression of log (concentration) vs. log (precipitation depth) for each individual sample using data for that site and time period so that a complete set of data was available as required for statistical analysis. Of a total of 6030 individual data points, 61 individual ion values were computed by using this procedure.

Results and Discussion

Regional Pattern in Precipitation pH. The geographic pattern of pH change from the 3 years of monitoring at eight sites is summarized in Tables I and II and in earlier maps by Hileman (*20*). In 1979–1980 pH ranged from 4.99 in western Minnesota to 4.33 in lower Michigan, but in 1981–1982 it ranged from 5.45 to 4.33. These results illustrate several caveats that must be considered when comparing the yearly results. The weather during each period may vary from what is considered to be typical. The laboratory (CAL) measurements represent analyses of composite samples without added preservatives over a week old, with variable transit and storage time before analysis. Weekly samples with no record of rain or chemistry correspond to weeks with no precipitation for that monitoring site.

The laboratory data comparing snow period to rain periods at these sites show increases in hydrogen ion of about 0.2 pH unit at the Minnesota and Wisconsin sites in the winter. The more acidic Michigan sites show almost no seasonal differences. The regional gradient in pH is evident at all times and includes the entire range of precipitation pH observed in northern Europe (*20–22*).

The pH values measured at CAL are consistently higher (less acidic) than those measured in the field monitoring sites, which indicates the dynamic nature of H^+ and the reactivity of substances in precipitation over time. These differences are attributable to biological activity, ion exchange, and reactivity of particulate materials such as soil particles with the reactions: $M_x(CO_3)_y$, M_xO_y, and $M_xSi_2O_8 + xzH^+ \rightarrow xM^{z+}$ where $M^{z+} = \sum Na^+, K^+, Ca^{2+}, Mg^{2+}, Al^{3+}, Fe^{3+}$ (*23*, *24*) over time. The analysis (Table II) of the differences between laboratory measurements of pH and the site pH shows (a) the differences at Lamberton, MN, are consistently greater by 0.7 pH unit than at the other locations and (b) for the seven locations not including Lamberton the average differences between CAL and site pH is 0.16 pH unit. This analysis uses all the observed differences between pH reported by CAL and site investigators pH, averaged by period and location. The increase in pH is equivalent to an approximate average reduction

Table III. Average Ion Concentration, Volume Weighted [Measured at CAL (in μequiv/L)], for the 2-year Period from Dec 1980 through Nov 1982 at All Eight NADP Sites

location	no. of samples	volume-weighted average ion concentration, μequiv/L										
		H^+	NH_4^+	SO_4^{2-}	NO_3^-	Cl^-	Ca^{2+}	Mg^{2+}	K^+	Na^+	$\Sigma(+)$	$\Sigma(-)$
Lamberton, MN	69	4	35	33	22	4	21	7	1	5	72	59
Marcell, MN	88	9	19	28	16	3	13	5	1	4	50	47
Fernberg, MN	85	12	18	31	16	3	10	5	1	3	49	48
Spooner, WI	71	14	31	42	22	3	14	4	1	3	67	67
Trout Lake, WI	93	19	20	37	19	2	10	3	1	2	56	58
Douglas Lake, MI	88	37	18	51	27	3	14	5	1	2	77	81
Wellston, MI	92	42	23	56	32	6	14	6	1	3	88	94
Kellogg, MI	81	46	25	64	30	4	14	5	1	3	94	98

of 12.5 μequiv/L hydrogen ion for all samples between collection and analysis by CAL (Table II). The highest changes were seen in samples from Lamberton, MN, and Wellston, MI, reflecting their proximity to cultivated land with a high content of alkaline soil substances. The lowest changes were seen in samples from Marcell, MN, and Trout Lake, WI, reflecting surrounding forest cover with low input of ion-exchanging and neutralizing substances.

The differences in pH are also related to the mechanisms of atmospheric washout which usually show an inverse relationship of ion concentration to precipitation rate (*9*). Negative slopes are expected for ion concentration vs. precipitation volume (or depth) relationships for gaseous and particulate components of the atmosphere including soil-derived ions (Table II). Highly significant, negative slopes are observed at all sites for all anions and cations except NH_4^+ and H^+. Ammonium ion shows negative slopes at all sites that are not significantly different from zero except at Lamberton, MN, and Douglas Lake, MI. Hydrogen ion, in contrast, shows all positive slopes that are significantly different from zero for CAL measurements while measurements by site operators show nonsignificant zero slopes except for Lamberton, MN. Here the slope is significantly nonzero, positive, and indicates the dynamic nature of $[H^+]$ in precipitation chemistry.

The data on seasonal differences in Table I show that the sites in Minnesota and Wisconsin with a more acidic pH during the snow period, December–March, indicate a potential to accumulate greater acid concentrations in the winter snowpack than during the rain period. The accumulation of acids in the snowpack at the three Michigan sites to 44 μequiv/L H^+ was more than double the H^+ concentration at the Wisconsin and Minnesota sites.

Is this pattern evident in Table I a long-standing or a relatively recent phenomenon? Estimates by Cogbill, Likens, and Butler (*14*, *15*) show all stations north and west of the lower peninsula of Michigan reporting a pH above 5.5 in 1955–1956. Stensland and Semonin (*13*) have suggested that neutralizing substances from transported dust during the mid-1950s might have contributed to the elevation of pH measurements in the east central states during those years, but their analysis shows no anomalous calcium content in the northern Great Lakes region at that time. Both reviews of the earlier data seem to agree that the precipitation pH measurements of 5.5 and above represent a rural regional "prealteration state" for Minnesota and Wisconsin up until the mid-1950s. The published results for the 1965–1966 and 1975–1976 periods (*13*, *15*) indicate that development of the region-wide gradient in pH has been a gradual one extending to Minnesota by the 1970s.

Seasonal and Geographic Pattern in the Ionic Composition of Acid-Forming Substances. Because precipitation pH is a measure of the resultant proton concentration after numerous reactions between acid-forming precursors, ion exchange, and neutralization reactions with the specific mix of gaseous and particulate materials washed out of the atmosphere during a given precipitation event, the concentrations of the resultant reaction products, both anions and cations, need to be considered at each site. Strong acid precursor emissions result from fossil fuel combustion and ore smelting, causing strong acids to dominate the ionic composition of precipitation (*26*). Strong acids result from oxidation and hydration reactions in the atmosphere: SO_x, $NO_x \rightarrow H_2SO_4$, HNO_3 (*25*, *26*). The molar ratio of sulfate to nitrate ions in GLS precipitation ranges from an average low value of 0.8 occurring at Lamberton, MN, to a high of 1.12 at Kellogg, MI, and reflects the relative increase in sulfur oxide emissions in the east. These ratios compare with values 0.72 and 1.1 for Minnesota and Michigan, respectively, derived from state emission inventories for 1975–1978 (*26*). These major anion concentrations are indicative of strong acid precursors across the region. Individual site averages are given in Table III. The major cations, in addition to H^+ in descending order of average concentration are NH_4^+, Ca^{2+}, Mg^{2+}, K^+, and Na^+.

Ammonium (NH_4^+) ion is an important and interesting reaction product of acid aerosols with gaseous ammonia, $H_2SO_{4(s)} + NH_{3(g)} \rightarrow (NH_4)_2SO_{4(s)}$ (*11*, *27*). Ammonia neutralizes H^+ in precipitation, but then ammonium ion serves as a major contributor to the acidic inputs to surface water due to microbial activity (nitrification) that occurs in surface water: $NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + H_2O$ (*24*). In Table III, ammonium ion with hydrogen ion are the dominant cations, 66 ± 5%. These, with the base cations (Ca^{2+}, Mg^{2+}, Na^+, and K^+) are in ionic balance with sulfate, nitrate, and chloride anions at seven of the eight sites. An imbalance occurs at Lamberton, MN, where a 18% deficit in anions is due to unmeasured HCO_3^- and OH^- (*23*). The average concentration of the sum of base cations is 23 ± 4 μequiv/L for all sites (Table III) and results from ion-exchange and acid neutralization reactions with H^+ and from the washout and weathering of soil particles (*23*).

Both the geographical and seasonal patterns of volume-weighted average concentrations of ions in precipitation from atmospheric washout can be evaluated by using plots of the mean concentrations of ions from the eight monitoring sites as a function of time through a two-way analysis of variance (location by period). The data for the statistical analyses are for the 2 years of weekly composite samples for the period Dec 1980 through Nov 1982. Although data collection at some stations started in 1979, only the years with complete data from all eight stations could be used. To provide data for comparable periods, the 2 years were divided into six 4-month periods corresponding to the snow period (December through March), and two rain periods, spring–summer (April through July) and summer–fall (August through November).

Plots of the standardized means for concentrations

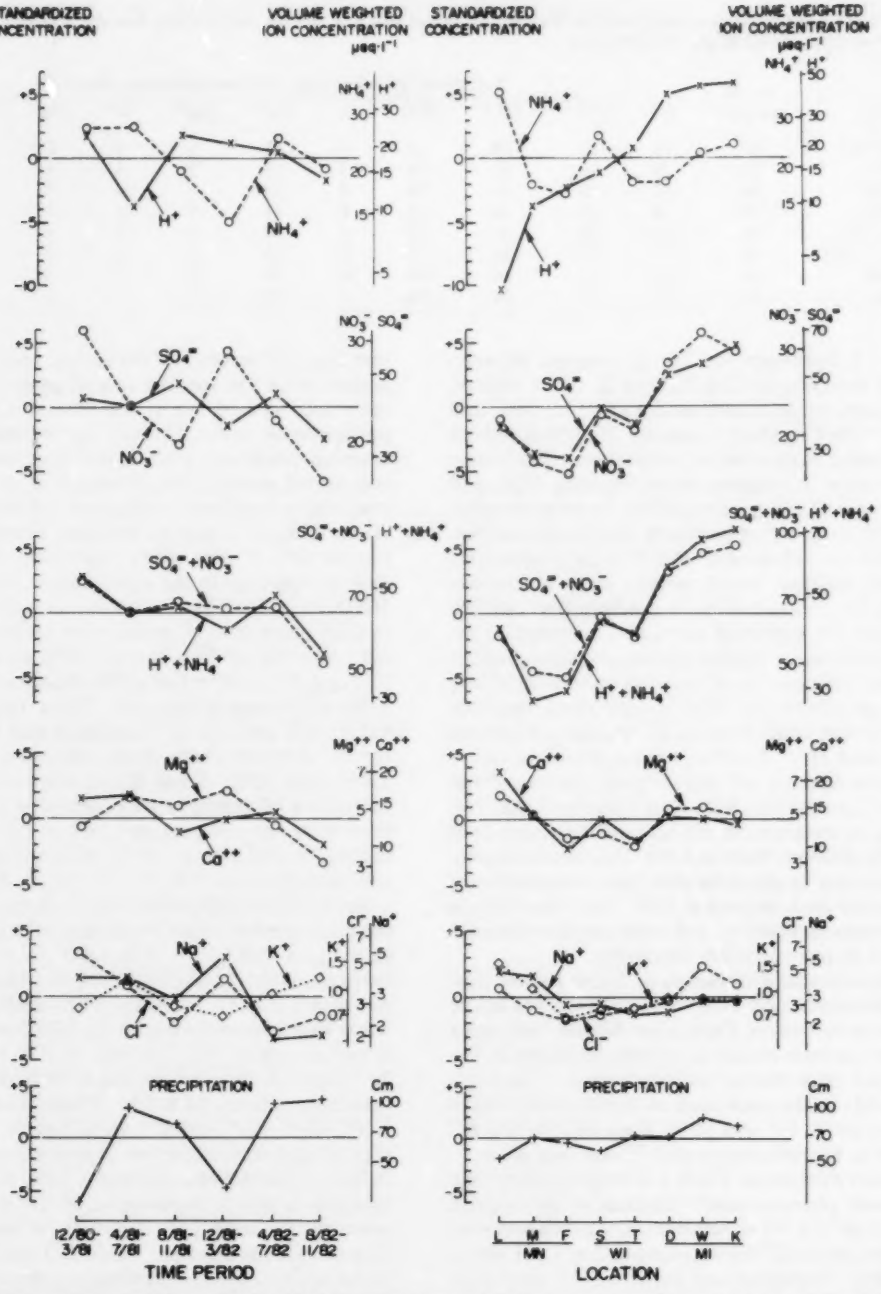

Figure 1. Standardized mean concentration (volume weighted, μequiv/L) of ionic substances in precipitation for six consecutive 4-month periods (2 years) beginning Dec 1980 to Nov 1982, showing seasonal patterns and regional gradient in concentrations for eight monitoring sites from southwestern Minnesota to south central Michigan.

(Figure 1) allow comparison of the mean responses relative to their pooled standard error where

the standardized mean (for the period or site, i) = mean (for the period or site i) − overall mean
standard error (of the mean for the period or site i)

The standard error of the mean is based on the mean square error from the analyses of variance and is assumed to be equal to the standard error of the overall mean. In Figure 1, the left axis is in units of the standardized mean while the right axis is in units of log concentrations in microequilivents per liter. Differences of about 3 units in the standardized means are significant at the 5% level (using Tukey's HSD multiple comparison procedure (28)).

The NO_3^- concentrations illustrate a consistent but opposite seasonal pattern to K^+ concentrations and precipitation depth while Ca^{2+} and Mg^{2+} concentrations illustrate seasonal fluctuations of no statistical significance. The sum of $[SO_4^{2-}] + [NO_3^-]$ closely parallels the sum of $[H^+] + [NH_4^+]$, which is consistent with the observations of Brosset (27) and others (7, 25, 26), and indicates the dominance of anthropogenic sources of total atmospheric acidity in Europe and North America.

The model used for the two-way analysis of variance is

resultant variation in response =
variation in response by location + variation in response by period + variation due to random error

Table IV. Analysis of Variance (Two Way) Giving Significance Level for Differences in Ion Concentrations, Depositions, and Precipitation between Locations and Periods

	significance level for differences			
	concentrations		depositions	
ion	period	location	period	location
H^+	0.0014[a]	<0.0001[c]	0.0004	<0.0001[c]
NH_4^+	<0.0001[c]	<0.0001[c]	<0.0001[c]	0.031[a]
SO_4^{2-}	0.045	<0.0001[c]	<0.0001[c]	<0.0001[c]
NO_3^-	<0.0001[c]	<0.0001[c]	0.0001[c]	<0.0001[c]
Cl^-	0.0008[c]	0.085	0.0031[b]	0.0015[b]
Ca^{2+}	0.077	0.012[d]	<0.0001[c]	0.0080[a]
Mg^{2+}	0.0042[b]	0.11	<0.0001[c]	0.040[a]
K^+	0.21	0.16	<0.0001[c]	0.11
Na^+	0.0002[c]	0.24	0.0018[b]	0.27
$H^+ + NH_4^+$	0.0032[b]	<0.0001[c]	<0.0001[c]	<0.0001[c]
$SO_4^{2-} + NO_3^-$	0.0026[b]	<0.0001[c]	<0.0001[c]	<0.0001[c]
precipitation	<0.0001[c]	0.18		

[a] Significance level is <5%. [b] Significance level is <1%. [c] Significance level is <0.1%.

The significant differences by location and period are summarized in Table IV by using an analysis of variance *F* test (*27*). These results show (a) that consistent annual patterns in ion concentrations exist across the region, (b) that the variations in dominant anions (SO_4^{2-}, NO_3^-) and acid-formed cations (H^+, NH_4^+) and their sums are significantly larger than would occur by chance, and (c) that no patterns of statistical significance in the differences in ion concentrations of Ca^{2+}, Mg^{2+}, Na^+, K^+, and Cl^- between locations are larger than would be expected by chance.

The analysis of variance for differences in period and location across the GLS sampling sites (Table IV) shows that the pattern for variation in H^+, NH_4^+, SO_4^{2-}, and NO_3^- and their sums has a probability of <1% of being random. The gradient in acidic reactants and products is consistent with the regional pattern in sulfur and nitrogen oxide emissions from sources in the region (*29*).

While a minor difference exists for Ca^{2+}, no significant differences are found across the region for Cl^-, Mg^{2+}, K^+, or Na^+ despite the location of the Lamberton, MN, site in an agricultural region near alkaline soils. Lamberton, MN, exhibits the highest Ca^{2+} and NH_4^+ concentrations, and both Spooner and Kellogg exhibit higher than average concentrations of NH_4^+ (Figure 1). All of these sites are in agricultural areas where volatile, anhydrous ammonia is extensively used in field applications for fertilizer, although the Spooner site has forest to the north and east. In contrast to the drought-period results reported by Stensland and Semonin (*13*), the high calcium concentrations at Lamberton, MN, suggest that during periods of normal precipitation the effects of soil dust from agricultural activity are relatively localized. These results are consistent with the limited cross-regional data for Minnesota obtained by Thornton and Eisenreich (*10*) and Munger (*11*), who reported a sharp decrease in cation concentrations from the Dakotas across Minnesota. Their data show that the highest values for calcium in precipitation occurred during periods when there existed extensive bare soil (especially in the winter) from agricultural activity. Verry (*23*) also has reported results for winter samples at Marcell, MN, to be affected by lack of snow cover and soil conditions upwind to the west. For the lower concentrations of SO_4^{2-} and NO_3^- at the western and northern sites in the GLS region, the concentrations of $Ca^{2+} + Mg^{2+}$ exceed H^+ but remain at less than 30% of $SO_4^{2-} + NO_3^-$ and show the important influence that ion-exchange and neutralization reactions can have on the resultant pH. For the year as a whole, however, elevated concentrations of Ca^{2+} and Mg^{2+} from alkaline dust are not evident either at Marcell, MN, or at Spooner, WI, both of which are just beyond the edge of intensive agriculture.

Seasonal and Geographic Pattern in Wet Deposition. Since the potential for adverse effects on terrestrial resources is thought to be controlled by the total deposition of reactive substances (concentration × precipitation amount plus dry deposition), the average annual wet deposition of acidic and neutralizing substances is of major interest (Table V). Dry deposition would increase these values by 10% to more than 100%, depending upon many factors including atmospheric concentrations and conditions, receptor surface properties, and proximity to emission sources (*5*, *24*, *30*).

Even more than the above results for concentration show, total ionic deposition, similarly plotted by using standardized means, shows a strong seasonal pattern (Figure 2) and higher statistical significance (Table IV). The spring–summer and summer–fall precipitation peaks (Figure 1) in the region produce similar peaks in the deposition of other important chemical species during these periods, despite the higher average winter concentrations at some sites. The greater deposition of ammonium ion (NH_4^+) compared to H^+ in the central and western sites is evident in the deposition data for both location and time plots. The identical pattern observed for the sum of ($SO_4^{2-} + NO_3^-$) deposition and the sum of ($H^+ + NH_4^+$) deposition (Figure 2) shows, however, that sulfur and nitrogen oxides are the major source of acidic reactants in the atmosphere of this region.

The relative difference in wet deposition of SO_4^{2-} and NO_3^- from the western sites to the eastern sites, comparing Lamberton, MN, to Kellogg, MI, is 40% and 55%, respectively. The west to east regional gradient in wet deposition is shown by the ratios of SO_4^{2-}, NO_3^-, and $SO_4^{2-} + NO_3^-$ for Minnesota/Michigan sites and are 0.47, 0.53, and 0.49, respectively. These ratios can be compared with those derived from state emission inventories (*26*) of SO_2 and NO_2 (1975–1978) and are 0.30, 0.55, and 0.38, respectively. The nitrogen oxide emission/nitrate wet de-

Table V. Yearly Ion Deposition [Measured at CAL (in equiv/(ha•year))] Based on the 2-year Period from Dec 1980 through Nov 1982, Using Weekly Composite Samples from the Eight Precipitation Monitoring Sites

		ion deposition, equiv/(ha-year)									
location	precip, cm	H^+	NH_4^+	SO_4^{2-}	NO_3^-	Cl^-	Ca^{2+}	Mg^{2+}	K^+	Na^+	$H^+ + NH_4^+$
Lamberton, MN	62	23	220	210	140	23	130	43	9	29	240
Marcell, MN	78	72	150	220	130	20	98	35	8	30	220
Fernberg, MN	71	85	120	220	110	20	73	32	6	23	210
Spooner, WI	72	99	220	300	160	19	100	31	6	21	320
Trout Lake, WI	86	170	170	310	170	20	86	29	6	16	340
Douglas Lake, MI	72	260	130	370	200	24	100	38	8	18	390
Wellston, MI	88	370	200	490	280	53	120	49	9	25	570
Kellogg, MI	83	380	200	530	250	36	120	45	9	23	590

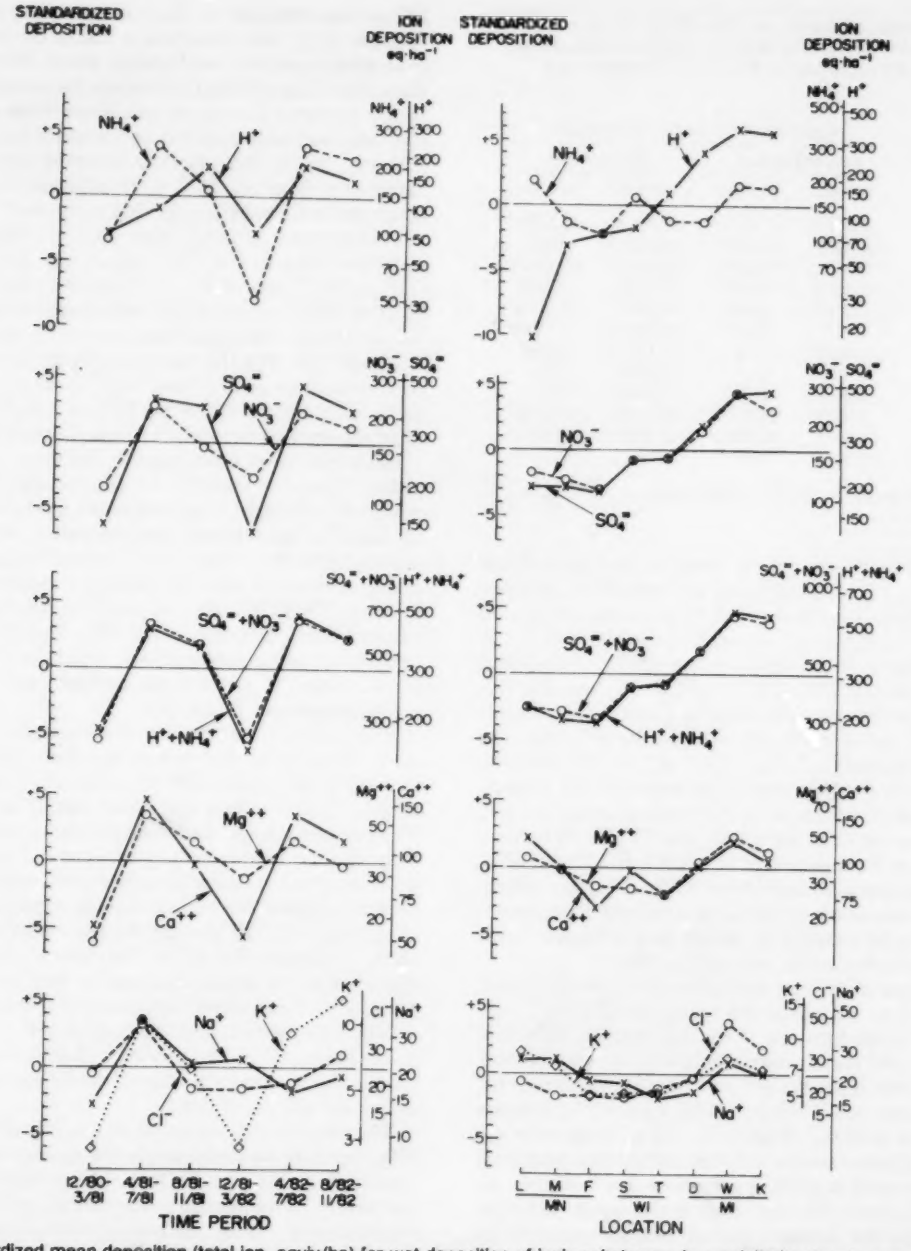

Figure 2. Standardized mean deposition (total ion, equiv/ha) for wet deposition of ionic substances in precipitation for six consecutive 4-month periods, Dec 1980–Nov 1982, showing strong rain period peaks and regional gradient in wet deposition from southwestern Minnesota to south central Michigan.

position ratios are in good agreement but sulfur wet deposition in Minnesota is greater than predicted from Minnesota sulfur oxide emission sources alone.

Comparison of Ca^{2+} deposition (Table V) with results for the middle 1950s (*13*) shows there has been little change since that time. The locational variation in deposition of Mg^{2+}, Ca^{2+}, Na^+, K^+, and Cl^- differ from random at a probability of less than 5%, and the acidic precursor products differ from random at less than 0.1% probability and show a strong positive increase with increased emissions in the east (*26*, *29*).

The possible effect of precipitation anomalies on calculated deposition amounts during the 1979–1982 period was examined by comparing the measured amounts of precipitation at each site with the 40-year averages at the site or at a nearby U.S. Weather Service station. Precipitation amounts were, statistically, very close to the normal with the exception of above normal precipitation at the Douglas Lake, MI, monitoring site during the April–Oct 1981 period. No other extreme wet or dry periods occurred.

Comparisons with Other Regions and Surface Water Chemistry. The data in Table VI show total wet deposition calculations for several sites outside of the Great Lakes States, allowing comparison with four other regions, two of them remote from emissions sources. Even the most westerly sites of the GLS region (Table V) show total quantities of acidifying substances appreciably greater than those of the two remote North American mountain regions. Several major industrial sources of SO_2 occur within a

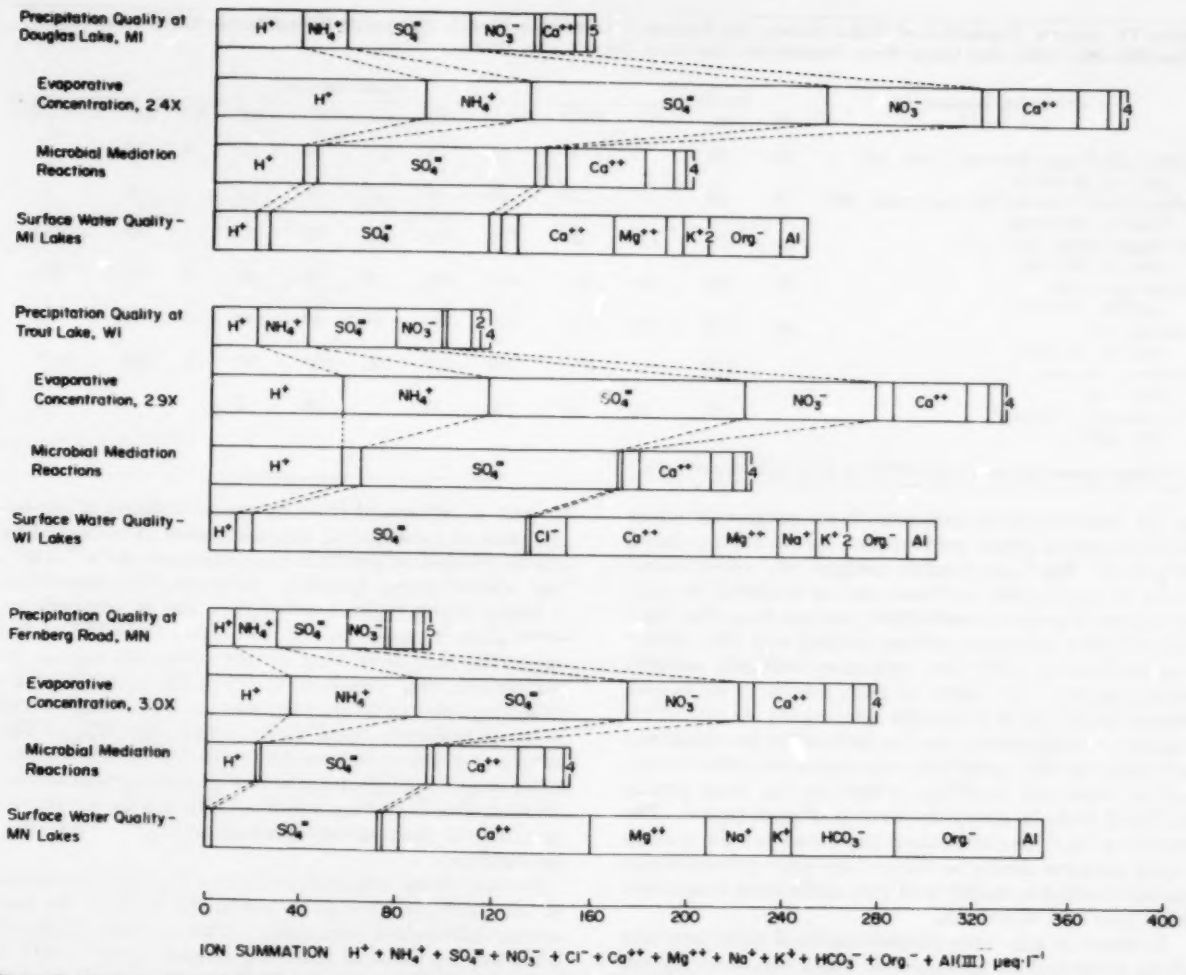
Precipitation Quality at Douglas Lake, MI
Evaporative Concentration, 2.4X
Microbial Mediation Reactions
Surface Water Quality - MI Lakes
Precipitation Quality at Trout Lake, WI
Evaporative Concentration, 2.9X
Microbial Mediation Reactions
Surface Water Quality - WI Lakes
Precipitation Quality at Fernberg Road, MN
Evaporative Concentration, 3.0X
Microbial Mediation Reactions
Surface Water Quality - MN Lakes
0 40 80 120 160 200 240 280 320 360 400
ION SUMMATION H+ + NH4+ + SO4= + NO3- + Cl- + Ca++ + Mg++ + Na+ + K+ + HCO3- + Org- + Al(III) μeq·l-1

Figure 3. Annual average ion concentrations in precipitation at three monitoring sites in the western Great Lakes States showing the regional gradient between sites and expected concentrations after concentration by evaporation and microbial mediation reactions (see text) in comparison with the observed average water concentrations for eight weakly buffered lakes in each of the precipitation monitoring regions. Vertical bars indicate concentration boundary values for all ionic components, and numbers within the bars indicate overlap for low or zero ion concentrations.

300-km radius of Glacier National Park and may have contributed to the moderate levels of SO_4^{2-} and H^+ deposition observed at this otherwise remote site.

Of the three sites representing the Northeastern United States (Table VI), Aurora, NY (near Cornell University), an agricultural site, located downwind from major industrial areas in western New York, Ohio, and Pennsylvania, has the highest wet deposition of acid-forming substances of any U.S. site considered in this study, about 80% more than the Kellogg site in central Michigan. Because of higher precipitation, Hubbard Brook, NH, and Huntington, NY, show concentrations of acidic substances that, while similar to the values measured for the three Michigan sites, are higher in deposition.

The Narbuvollen site (Table VI), in east central Norway, an area similar to the northern GLS region with pine, spruce, and birch forests (*9*) and crystalline bedrock (*3*, *30*), warrants further comparative study. Precipitation there averages about 42 cm annually (*3*), less than in the relatively dry regions of Minnesota, Wisconsin, and Michigan, and the wet depositions of acidic substances there measure lower amounts. However, in the vicinity of the Narbuvollen site significant alterations of water quality and fish populations have been reported and were attributed to the acidic inputs from the atmosphere (*32*).

The observed difference in aquatic effects, since the magnitude of wet-acidic inputs in Scandinavia is similar to the GLS, may be attributed to the differences in the duration of those inputs, hydrology (*31*), weathering rates of bedrock and soils (*3*), and other factors (*5*). Surface water quality alterations have been reported on a moderate scale in Norway for 30–60 years, and acidic deposition probably has occurred throughout this century (*3*). The evidence reviewed here indicates that region-wide, wet-acidic inputs to the GLS have had a duration in the order of only 20–30 years, but local emission sources using high-sulfur coal, ore smelting, and ore-sintering activities might have influenced some weakly buffered lakes at a much earlier time, without detection (*34*, *35*).

The indications that present acidic atmospheric inputs have significantly altered the surface water chemistry of weakly buffered lakes in the GLS can be seen by comparisons of the ionic composition of precipitation across the region with those of the resultant lake water (*8*, *9*, *31*, *36*, *37*). The changes in water chemistry as precipitation is transformed into surface water during the inflow process can be complex involving physical, chemical, and biological processes and are illustrated in Figure 3 by using a stepwise mechanism (*5*, *33*). Concentration by evaporation (*5*, *38*) of ionic components, such as chloride, in precipitation up

Table VI. Annual Deposition of Major Anions and Cations Measured in Weekly Composite Precipitation Samples at NADP (Dec 1980–Nov 1982) and Other Sites Outside the Northern Great Lakes States

site name; location (lat., long.)	N	precip cm	equiv/(ha·year)									
			H^+	NH_4^+	SO_4^{2-}	NO_3^-	Cl^-	Ca^{2+}	Mg^{2+}	K^+	Na^+	$H^+ + NH_4^+$
Denali (McKinley National Park), AK; N63°43′, W148°58′	73	29	9	6	28	7	13	10	12	5	16	16
West Glacier (Glacier National Park), MT; N48°31′, W113°60′	73	68	52	23	89	43	14	30	17	5	14	75
Hubbard Brook, NH; N43°57′, W71°42′	95	124	570	130	570	290	62	70	37	5	58	710
Huntington, NY; N43°58′, W74°13′	94	100	420	150	490	250	28	80	30	6	27	570
Aurora, NY; N42°44′, W76°40′	90	78	560	170	590	280	40	80	30	5	31	730
Birknes, Norway;[a] N58°, E8°		148	1000	620	1100	600	920	130	180	44	780	1600
Narbuvollen, Norway;[a] N62°, E11°		42	92	46	130	54		46	8			140

[a] Mean annual values of 1977–1979 for daily bulk samples (*3*).

to 2–4 times can occur and varies from east to west across the GLS region, giving the predicted concentrations shown (Figure 3). For more reactive components, microbial activity or mediation reactions can be modeled by stoichiometry of oxidation–reduction reactions involving NH_4^+ (nitrification processes adding acidity) and NO_3^-/SO_4^{2-} (denitrification/reduction processes reducing acidity) where reaction of 1 equiv of each results in no overall change in acidity or alkalinity content (*24*, *33*, *36*). This reaction stoichiometry is used to account for the significant reduction in NH_4^+ and NO_3^- concentrations, after evaporation, observed in surface water for the most weakly buffered lakes in the northern area of each region. The resulting ionic concentrations predicted for the surface water compare closely to the average ionic concentration values observed in weakly buffered, acidic lakes in northern Michigan and Wisconsin.

Increases in lake water concentrations of metal ions over those predicted by atmospheric input can occur by ion exchange, dissolution of sediment components, and weathering of soils and land use in the watershed yielding concentrations of base cations, aluminum, and corresponding bicarbonate, chloride, and organic anions (*5*). These data (Figure 3) indicate that, given the present differential in acidic inputs, the lake basins in the upper GLS must presently supply at least 20–60 μequiv/L acid-neutralizing substances (alkalinity) and ionic exchange substrate annually to precipitation inflow so that the pH may increase to 6.5 which is the minimum pH value considered safe for an abundance of freshwater aquatic life (*39*).

Summary and Conclusions

In a regional assessment of precipitation chemistry, care must be taken to consider a wide variety of potentially significant variables (*5*). Year-to-year differences in climatic trends, as well as potential local influences of topography, vegetation, and land use, may need to be evaluated. In this paper, local anomalies in precipitation composition have been considered in relation to long-term averages, both seasonal and annual. The effects of local sources of pollutants and local agricultural influences have been either minimized by site selection or treated systematically as part of the experimental design and analysis.

Despite variation in the wet deposition of substances during the 2–3-year study period, three conclusions can be drawn that are relevant to the aquatic resources at risk from acidic deposition in northern Michigan, Wisconsin, and Minnesota. First, the regional pH gradient from east to west is influenced little by concentrations of ion-exchanging or neutralizing soil substances as indicated by relatively constant resultant concentrations of Ca^{2+}, Mg^{2+}, Na^+, and K^+ in precipitation. Although NO_3^- deposition is higher in this region compared to that of relatively remote sites, it ranges in wet deposition from 140 to 250 equiv/(ha·year) from west to east across the region. In comparison, SO_4^{2-} ranges from 210 to 530 equiv/(ha·year) reflecting total emission increases across the region and is in approximate equal molar ratios with NO_3^-. The pattern in pH must be considered with $[NH_4^+]$ in assessing anthropogenic acid/precursor sources and implications for acidification of surface waters. Both can be attributed primarily to the resultant gradient in $SO_4^{2-} + NO_3^-$ concentrations.

Second, these results show total wet-acidic deposition at the Michigan sites to be similar to those of the east central Adirondack region and portions of New England, while wet deposition of acidifying substances ($H^+ + NH_4^+$) in Michigan, Wisconsin, and Minnesota exceeds that of the interior of Norway and Sweden. Wet deposition of acidifying substances in Minnesota appears to be 2–10 times greater than that of unimpacted remote North American continental sites, but less than most sites where impacts have been observed. In northern Michigan and north central Wisconsin where there is close chemical correspondence between precipitation and weakly buffered surface water composition, acidification is observed. Studies of similarities and differences in the receiving landscape may be required to determine whether a continuation of the present loadings is inducing effects on resources similar to those observed in Scandinavia. The hydrology of lakes (*31*) in the Great Lakes region, differences in soil weathering rates (*24*), and the careful evaluation of historical change and loadings must be taken into account.

Finally, it may be possible to evaluate the regional importance of acidic deposition observed in the western Great Lakes States through comparisons with effects on aquatic chemistry and biotic resources now reported in areas of central Norway. The Norwegian sites have similar climate, bedrock, and soils and are receiving similar (or less) rainfall and wet-acidic deposition amounts. Surface water quality changes that are thought to have induced a decline of the local fishery in the most sensitive watersheds have been observed in the Norwegian study site. The apparent difference in biotic effects from central Norway to the Great Lakes States may be due to incomplete surveys in the Great Lakes States, differences in watershed charac-

terization, and the longer period of acidic deposition in Scandinavia.

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Registry No. NH_4^+, 14798-03-9; H^+, 12408-02-5; Ca, 7440-70-2; Mg, 7439-95-4; K, 7440-09-7; Na, 7440-23-5.

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